

PATENT SPECIFICATION

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(54) DURABLE ANTISTATIC FINISHING OF SYNTHETIC TEXTILES

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the durable antistatic finishing of synthetic fibers or textiles by fixing compounds containing antistatically active groups on the surface of the fibers.

It is known that the high static charge acquired by synthetic fibers causes serious difficulties in the processing of the fibers and detracts, in use, from the properties of textiles made from these fibers. Problems manifest themselves particularly in the case of staple fibers on various carding machines, on draw-frames and on flyers and in finishing operations, where textiles of synthetic fibers can only be handled with difficulty, due to static electrification. Finally, problems also arise in wear as a result of garments clinging to the body, and because of increased pilling.

Various antistatic agents which are applied to the textile material by specific methods and which in most cases are surface-active and hence increase the conductivity of the fiber surface, have been developed in order to solve this problem. These products are generally antistatic agents which can be washed off. However, the trend is toward the provision of durable antistatic agents.

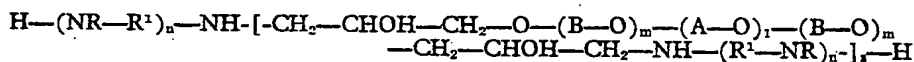
Antistatic agents which can be used on synthetic macromolecular substances and which to a certain degree are durable include, for example, sulfonates of substituted vinyl polymers and alkyl polymers (British Patent 786,953), polyhydric alcohols and polymers of unsaturated monocarboxylic acids or dicarboxylic acids (German Laid-Open Specification 1,032,713), polyethylene glycol acrylates (German Laid-Open Specification 1,028,524), water-insoluble amine salts of polystyrenesulfonic acids (U.S. Patent 2,676,896), fatty acid esters of hexitol anhydrides and their oxyalkylene derivatives (U.S. Patent 2,628,176), quaternary ammonium compounds substituted by fatty acid alkylamido groups and alkeneoxy groups (U.S. Patent 2,836,517), copolymers of monoalkoxypolyethylene glycol acrylates or methacrylates with acrylamides or methacrylamides or glycidyl methacrylates (U.S. Patents 2,839,430 and 2,839,431) and quaternary salts of substituted polyacrylic or polymethacrylic acid aminoesters (German Laid-Open Specification 1,021,824). It is also known that textiles can be rendered antistatic by causing reaction products of alkylenepolyamides with epichlorohydrin to react, on the surface of the textiles, with chlorohydrin ethers of polyethylene glycols.

However, hitherto there has not yet been an antistatic finish for textiles which is sufficiently resistant to laundering. In addition, many of the antistatic agents mentioned have proved incompatible with finishing agents which may be required additionally; for example, some of the antistatic agents tend to break emulsions. Further, the finished goods frequently have a hard hand.

The present invention seeks to provide an antistatic finish which is genuinely resistant to laundering, does not interfere with the use of other finishing agents and in addition does not adversely influence the hand of the goods.

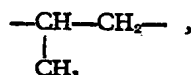
According to the present invention there is provided a process for the durable antistatic finishing of synthetic fibers or textiles by fixing a compound containing anti-

statically active groups on the surface of the fibers, wherein a compound of the formula I



where A is n-butylene of the formula $(-\text{CH}_2-)_4$,

B is alkylene of the formula $-(\text{CH}_2)_z-$ or



R is hydrogen or an aliphatic radical of 1 to 6 carbon atoms, and the radicals R can differ if n is greater than 1,

R¹ is alkylene of 2 to 6 carbon atoms,

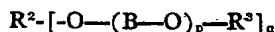
l = 5—100,

m = 0—30,

n = 1—4 or, if R¹ = C₂H₅, 1—20 and

z = 1—10

is allowed to react, on the fiber, with a compound of the formula II

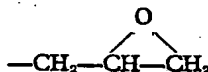


where B has the meanings given above,

p = 0—30,

R² is a 2-valent to 6-valent aliphatic or cycloaliphatic branched or unbranched hydrocarbon radical of 3 to 13 carbon atoms,

R³ is a radical of the formula $-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{Cl}$ or



and

q is an integer from 2 to 6.

The antistatic finish according to the invention prevents practically any static charge on synthetic fibers or textiles and is very durable to laundering, sometimes more durable than any previously known antistatic finish.

Examples of synthetic fibers which can advantageously be provided with the finish according to the invention are fibers of polyethylene, polypropylene, vinyl chloride polymers or vinylidene chloride polymers, polyurethanes and especially polyesters, acrylonitrile homopolymers and copolymers, and polyamides.

The term "textiles" is intended to include sheet-like structures consisting of filaments or fibers, such as woven fabrics, knitted fabrics and non-woven fabrics.

The term "fixing" means bringing about a reaction in such a way that the components of the finishing agent either crosslink with one another and are deposited in an insoluble form on the surface of the fiber or that they react with functional groups of the fibers, if such groups are present, and in this way are chemically bound to the fibers. Depending on the reactive system in question, such reactions can be brought about either by storing the finished and optionally dried goods at ambient or slightly raised temperature or, as is most frequently the case, by heating the finished goods to elevated temperatures, for example to 70—200°C.

Groups which have an antistatic action are polar groups which, when present on the surface of the substrate, entirely or largely prevent the surface from acquiring a static charge. In the case of the present invention, these groups consist of the hydroxyl groups and ether groups of the chlorohydrin groups or epoxide groups which have undergone reaction. The action of the groups can be assisted by polyethylene oxide blocks or polypropylene oxide blocks $(\text{B}-\text{O}-)_m$ and $(\text{B}-\text{O}-)_p$, with m and p independently of one another being integers from 0 to 30 preferably 0 to 20. Such $(\text{B}-\text{O}-)$ blocks, if present at all, can be contained in the compound I or in the compound II or in both. The amino groups of compound I also assist the antistatic action.

The compounds of the formula I can, for example, be prepared as follows: The starting material is polytetrahydrofuran with a degree of polymerization of 5—100, preferably 10—60.

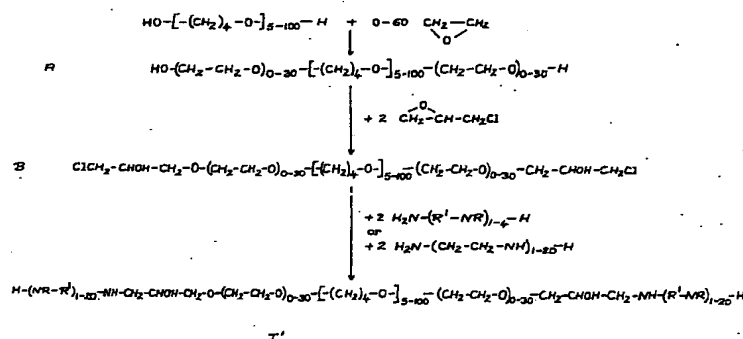
This polyether can first be oxyethylated or oxypropylated at both chain ends with up to 30, preferably up to 20, moles of ethylene oxide or propylene oxide and can then be reacted with epichlorohydrin, or can be directly reacted, that is to say without oxyethylation or oxypropylation, with epichlorohydrin, at both chain ends, to give the bis-chlorohydroxypropyl ether. This reaction may be carried out by conventional methods, for example by slowly adding epichlorohydrin to the undiluted polyether at about 70 to 80°C in the presence of catalytic amounts of boron fluoride etherate. If subsequently sodium hydroxide solution, for example, is added, the bis-epoxide is obtained in a known manner from the bis-chlorohydrin.

The bis-epoxide or bis-chlorohydrin is reacted with 1.1 to 2, preferably 1.3 to 1.7, moles of an aliphatic polyamine with 2 to 5 amino groups and 2 to 6, preferably 2 or 3, carbon atoms between each pair of amino groups, or with such amounts of polyethyleneimine of degree of polymerization up to 20 that the amino groups are present in an excess of about 1 to 20, preferably 1.3 to 5, times the chlorohydrin or epoxide groups. Examples of suitable polyamines are ethylenediamine, propylenediamine, hexamethylenediamine, diethylenetriamine, dipropylenetriamine, dihexamethylenetriamine, triethylenetetramine, tetraethylenepentamine and bis-(3,3-amino-propyl)-methylamine. This reaction also may be carried out by conventional methods, for example in butanol as the diluent at approx. 110°C, or without solvents at 100 to 130°C.

The resulting molecular weight depends on the molar ratio of the components employed. With a ratio of bis-epoxide (or bis-chlorohydrin) to diamine of 1:1.1, z in the formula I is about 10, with a ratio of 1:1.5 it averages 2 and with a ratio of 1:2, $z=1$. In the case of polyamines with more than 2 amino groups, this pattern may be shifted somewhat but on average not significantly more than 2 amino groups should react per mole of polyamine.

In order to make the reaction product, which is a compound of the formula I with $z=1-10$, preferably 1-5, readily water-soluble, the mixture is neutralized to pH 5.5 to 7 with a relatively readily volatile and preferably weak acid, such as formic acid or acetic acid. The goods to be finished are impregnated with this solution, which is diluted to suit the particular requirements, separately from, or preferably together with, a bath containing the solution of a compound of the formula II.

The entire reaction scheme for the preparation of compounds of the formula I, using polytetrahydrofuran as the starting component, is as follows:

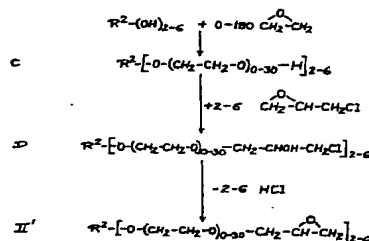


The formulae I and I' are idealized for simplicity inasmuch as they show products in which only one or two amino groups per mole of polyamine have reacted with one chlorohydrin or epoxide group. In reality one is of course always dealing with mixture which, whilst they contain the product corresponding exactly to the formula I', also contain products in which more than two amino groups have reacted per mole of polyamine.

The compounds of the formula II can be prepared analogously to the first, or the first two, stages of the compounds of the formula I, i.e. reaction with epichlorohydrin (optionally preceded by oxyethylation or oxypropylation) and optional conversion of the chlorohydrin product to the epoxide. The starting material is an aliphatic or cycloaliphatic, branched or unbranched polyalcohol with 2-6, preferably 3 or 4, hydroxyl groups and 3-13, preferably 3-6, carbon atoms. Examples of suitable compounds are glycerol, 1,1,1-trimethylolpropane, pentaerythritol and sorbitol. Glycols

such as ethylene glycol, 1,4-butanediol and neopentyl glycol are also suitable, above all if the amine of the compounds of the formula I in total has more than two (primary and secondary) amino groups. However, if a diamine is concerned, polyols with more than two hydroxyl groups are to be preferred as starting materials for the compounds of the formula II.

The polyol can, like the polytetrahydrofuran employed as the starting substance for the preparation of the compounds of the formula I, first be oxyethylated or oxypropylated and then reacted with epichlorohydrin, or be reacted directly with epichlorohydrin. The amount of epichlorohydrin to be employed depends on the functionality of the polyol. The reaction scheme is the following:



As already mentioned, the impregnation of the goods to be finished with the solutions of the compounds of the formulae I and II, diluted to suit the desired substrate application and wet pickup, is preferably carried out in a bath. The two solutions can be mixed or partially reacted with one another immediately prior to use or—in the case of the chlorohydrins but not of the epoxides—at any desired point in time, that is to say even by the manufacturer. Care must be taken to ensure that the reaction does not progress to the point where the substance becomes water-insoluble. Accordingly, an advantageous variant of the process according to the invention is that compounds of the formula I are allowed to react with compounds of the formula II with



to the point where they still remain water-soluble, and are applied in this form to the fibers and fixed thereon by completing the reaction.

Because of the two components I and II being readily water-soluble, the finishing process is very simple. The textile goods are impregnated with the finishing bath, which is preferably aqueous, for example by padding, spraying, dipping, spreading or pouring so that an amount of product of 0.5 to 6% by weight, relative to the dry textile material, remains on the finished goods. Drying and fixing can take place at temperatures of 20 to 160°C, preferably 80 to 130°C, in one step or in two separate steps. The finished synthetic textiles display an outstandingly durable antistatic effect.

This treatment also makes the textiles soft and smooth so that the goods are distinguished not only by durable antistatic properties but also by a notable improvement in their hand. Furthermore, the textiles lend themselves to any further finishing operations practically as readily as without the antistatic finish according to the invention.

The following Examples 1 to 6 illustrate the production of the ingredients for use in the process of the invention. Examples 7 to 9 illustrate the process of the invention. In the Examples, the parts and percentages specified are by weight.

EXAMPLE 1.

Manufacture of a compound of the formula A

440 parts of ethylene oxide gas are introduced into 2,000 parts of polytetrahydrofuran and 2 parts of sodium methylate in an autoclave at 120°C and the mixture is stirred for one hour at this temperature. The yield of oxyethylated polytetrahydrofuran is quantitative.

EXAMPLE 2.

Manufacture of a compound of the formula B

277.5 parts of epichlorohydrin are added over 30 minutes, at 70 to 80°C, to 3,000 parts of polytetrahydrofuran of average molecular weight 2,000 which contain 15 parts of boron trifluoride etherate, and the mixture is then stirred for about 2 hours longer at 80°. The molar ratio of polytetrahydrofuran to epichlorohydrin is 1:2. The yield of bis-chlorohydrin is practically 100%.

EXAMPLE 3.

Manufacture of a compound of the formula I'

3,800 parts of polytetrahydrofuran-bis-3-chloro-2-hydroxypropyl ether (bis-chlorohydrin) of molecular weight 2,400 are added to 295 parts of dipropylenetriamine $\text{HN}(\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---NH}_2)_2$ in 596 parts of isobutanol at 100 to 110°C over 2 to 3 hours. The molar ratio of amine to bis-chlorohydrin is 1.5:1. The progress of the reaction is followed by titration with hydrochloric acid. After 6 hours at 110°C, the titer remains constant at 1.07 ml of 1N HCl per gram of reaction mixture when titrated in water against methyl red; the mixture is neutralized to pH 6 with glacial acetic acid and diluted water to a solids content of 30%.

EXAMPLE 4.

Manufacture of a compound of the formula C

660 parts of ethylene oxide gas are introduced into 200 parts of trimethylolpropane and 2 parts of sodium methylate in an autoclave at 120°C and the mixture is stirred for a further 1 to 2 hours at 120°C. The yield of oxyethylate is 100% of theory.

EXAMPLE 5.

Manufacture of a compound of the formula D

860 parts of the oxyethylate from Example 4 are neutralized with glacial acetic acid and 4.3 parts of boron fluoride etherate are added. 419 parts of epichlorohydrin are added to the mixture at 70 to 80°C over 40 minutes and the whole is stirred for 2 hours at 80°C.

The epoxide number of the reaction mixture is then 0.

EXAMPLE 6.

Manufacture of a compound of the formula II'

234 parts (representing a three-fold molar excess) of 50% strength aqueous sodium hydroxide solution are added to 857 parts of the compound of the formula D, obtained in Example 5, at 25 to 35°C and the mixture is stirred for 5 hours at room temperature. Thereafter sufficient water is added so that the sodium chloride which has precipitated just dissolves. The aqueous phase is separated from the organic phase. The latter consists of the tris-epoxide of the formula II'. The yield is 91% of theory.

EXAMPLE 7.

Polyester knitted goods weighing approx. 195 g/square meter are impregnated with an aqueous liquor which contains 80 g/l of a 30% strength aqueous solution of the product (formula I') of the reaction of the bis-3-chloro-2-hydroxypropyl ether of polytetrahydrofuran, of molecular weight 2,000, with dipropylenetriamine in the molar ratio of 1:1.5, and 20 g/l of the tris-glycidyl ether (formula II') of trimethylolpropane etherified with 10 moles of ethylene oxide; the goods are squeezed to a wet pickup of 100% on a padder and dried in a stream of air at 120°C in 3 minutes. The test specimens are laundered at 60°C, with addition of 2 g/l of a customary domestic detergent, using a customary domestic washing programme of total duration approx. 45 minutes.

The electrostatic charge on test specimens which have been conditioned for 24 hours at 60 to 65% relative humidity is measured as follows:

The woven fabric or knitted fabric strips (60 × 10 cm) which are to be tested are first reproducibly electrically charged by drawing the strip three times through a polished brass die of approx. 5 mm diameter. The die is inserted in a hard rubber insulant which is fixed to a stand by means of a rod fixed to its side. The woven fabric or knitted fabric strip which has been charged in this way is placed in an externally lacquered semi-cylinder made of sheet brass, which approximately represents a Faraday cage. This cage is also mounted on a stand by means of a rod of insulating material fixed to its side. The potential (in volts) which is recorded on an electrostatic voltmeter of Messrs. Rothschild, Switzerland, which is connected to this semi-cylinder by a conductor, is quoted as the test result.

The maximum charge is obtained with an untreated woven or knitted fabric. For example, for polyethylene, polyamide and polyacrylonitrile the figure obtained is about 1,800 to 2,200 volts. If the finish is completely antistatically effective, a value of 0 is obtained, that is to say no charging occurs.

	Chargeability (volts)				
	Number of launderings at 60°C				
	0	1	3	5	10
Untreated goods	-2,200	-2,000	-1,800	-1,500	-1,200
Finished goods	0	0	0	0	0

EXAMPLE 8.

Nylon-6,6 knitted goods weighing approx. 92 g/m² are finished, laundered and tested as in Example 7.

	Chargeability (volts)				
	Number of launderings at 60°C				
	0	1	3	5	10
Untreated knitted goods	-1,800	-2,100	-1,600	-1,400	-900
Finished knitted goods	0	0	0	0	0

EXAMPLE 9.

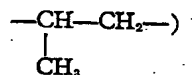
107 parts of polytetrahydrofuran di-chlorohydroxypropyl ether of molecular weight 2,000 are added dropwise to 9.8 parts of dipropylenetriamine in 100 parts of i-butanol and 4 parts of sodium hydroxide at 110°C and the mixture is stirred for 90 minutes at 110°C. 25 parts of the trischlorohydroxypropyl ether of trimethylolpropane are then added and the mixture is stirred for 1 hour at 110°C until the product gives a clear solution in water. The reaction mixture is neutralized with 12 parts of glacial acetic acid and diluted to 40% solids content.

15 Polyester knitted goods like those in Example 7 are finished with an aqueous liquor which contains 65 g/l of the said 40% strength aqueous solution, dried, laundered and tested, all as in Example 7.

	Chargeability (volts)				
	Number of launderings at 60°C				
	0	1	3	5	10
Untreated goods	-2,000	-1,600	-1,800	-1,200	-1,000
Finished goods	0	0	0	0	0

COMPARATIVE EXAMPLE.

20 495 parts of polypropylene oxide di-chlorohydroxypropyl ether (a compound resembling compounds of formula I except that A is



of average molecular weight 2,000 are added to 59 parts of dipropylenetriamine in 140 parts of i-butanol over 40 minutes at 110°C and the mixture is stirred for 6 hours at 110°C.

25 1 parts of the reaction mixture is then found to consume 1.3 parts of hydrochloric acid when titrated in water against methyl rest. 5.4 parts of glacial acetic acid are added and the mixture is diluted to 30% solids content with water.

Nylon-6,6 knitted goods like those in Example 8 are treated with an aqueous liquor which contains 80 g/l of a 30% strength aqueous solution of the reaction product mentioned and 20 g/l of the tris-glycidyl ether of trimethylolpropane, laundered and tested, all as in Example 7.

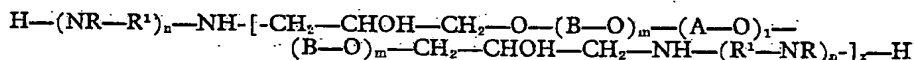
Chargeability (volts)
Number of launderings at 60°C

	0	3	1	5
Untreated goods	-2,100	-1,700	-1,900	-1,500
Finished goods	0	-100	-300	-350

Comparison of these figures with those in the Tables in Examples 7—9 shows that compounds of formula I in which A is n-butylene give more durable results than similar compounds in which A is other than n-butylene, in particular when it is 1,2-propylene.

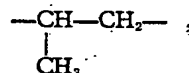
10 WHAT WE CLAIM IS:—

1. A process for the durable antistatic finishing of synthetic fibers or textiles by fixing a compound containing antistatically active groups on the surface of the fibers, wherein a compound of the formula I



15 where A is n-butylene,

B is alkylene of the formula $-(\text{CH}_2)_x-$ or



R is hydrogen or an aliphatic radical of 1 to 6 carbon atoms, and the radicals R can differ if n is greater than 1,

20 R¹ is alkylene of 2 to 6 carbon atoms,

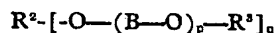
l = 5—100,

m = 0—30,

n = 1—4 or, if R¹ = C₂H₅, 1—20 and

z = 1—10

25 is allowed to react, on the fiber, with a compound of the formula II

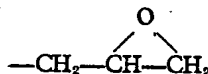


where B has the meaning given above,

p = 0—30,

30 R² is a 2-valent to 6-valent aliphatic or cycloaliphatic branched or unbranched hydrocarbon radical of 3 to 13 carbon atoms,

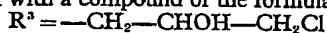
R³ is a radical of the formula $-\text{CH}_2-\text{CHOH}-\text{CH}_2\text{Cl}$ or



and

q is an integer from 2 to 6.

35 2. A modification of a process as claimed in claim 1, wherein a compound of the formula I is allowed to react with a compound of the formula II with



to the point that the product still remains water-soluble, and is applied in this form to the fibers and fixed thereon by completing the reaction.

3. A process as claimed in claim 1 or 2, wherein the compound of the formula I is obtained by reaction of a polytetrahydrofuran having a degree of polymerisation of 10 to 60 (or of an oxyethylation product thereof with up to 20 moles of ethylene oxide at both chain ends) with epichlorohydrin, reaction of the resulting bis-chlorohydrin (or of a bis-epoxide obtained therefrom by reaction with sodium hydroxide) with from 1.3 to 1.7 moles of an aliphatic amine of 2 to 5 amino groups and 2 or 3 carbon atoms between each pair of amino groups or with an amount of a polyethylene imine of a degree of polymerisation up to 20 such that the amino groups are present in an excess of 1.3 to 5 times the chlorohydrin (or epoxide) groups of the bis-chlorohydrin (or bis-epoxide), and neutralisation of the mixture to a pH of 5.5 to 7 with a relatively readily volatile acid.
4. A process as claimed in any of claims 1 to 3, wherein the compound of the formula II is obtained by reaction of an aliphatic or cycloaliphatic branched or unbranched polyol with 3 or 4 hydroxyl groups and 3 to 6 carbon atoms (or of an oxyethylation product thereof with up to 30 moles of ethylene oxide) with epichlorohydrin and optional reaction of the chlorohydrin product with sodium hydroxide to form an epoxide.
5. A process as claimed in any of claims 1 to 4, wherein the synthetic fibres or textiles are impregnated by means of a bath of an aqueous solution containing a compound of the formula I and a compound of the formula II and/or a water-soluble reaction product thereof, such that from 0.5 to 6% by weight of water-insoluble reaction product therefrom, relative to dry fibre or textile material, remains on the finished goods, and the impregnated material is dried and fixed in one or two steps at 80—130°C.
6. A process for the durable antistatic finishing of synthetic fibres and textiles, substantially as hereinbefore described with reference to any of Examples 7 to 9.
7. Synthetic fibres or textiles of polyester, polyamide or acrylonitrile homopolymer or copolymer finished by a process as claimed in any of claims 1 to 6.

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